

# Flame Retardant Elastomers for Chemical Protective Gloves

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## INTRODUCTION

BUTYL RUBBER, A copolymer of isobutylene and isoprene, has been commercially available since 1942. Different grades of butyl rubber available today are characterized by mole percent unsaturation (isoprene content) and Mooney viscosity. The halogenated butyls, chlorobutyl and bromobutyl, were introduced in the early 1960s and have been commercially available since then [1]. Suitably compounded and vulcanized butyl rubbers are characterized by low permeability, good resistance to heat, ozone and certain chemicals. They are used in tire inner tubes, tire curing bags and chemical protective clothing, including chemical protective (CP) gloves.

In chemical protective clothing applications, butyl rubber provides an excellent barrier to hazardous chemicals. However, butyl rubber is flammable, ignites readily, and burns vigorously if exposed to flame. Flame retardant (FR) additives commonly used in elastomers are antimony trioxide, organophosphates, zinc borate, brominated aromatics and ammonium polyphosphates [2]. This work discusses the use of additives to impart flame resistance to butyl rubber.

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Table 1. Rubber formulations.

Ingredients	Formulation, Parts		
	A	B	C
Chlorobutyl	100	100	100
Carbon black N339	38	38	33
Vistanex LM-MS	7.5	7.5	7.5
Sunpar 2280	—	5	—
Zinc stearate	1	1	1
Nickel dibutyldithiocarbamate	1	1	1
Carabowax 3350	1	1	1
Zinc oxide	3	3	3
END-75	1	1	1
Benzothiazyl disulfide	1.25	1.25	1.25

## EXPERIMENTAL

### Materials

Formulations of the rubber compounds investigated in this study are given in Tables 1 and 2: A, B and C contain no FR additives, and AF, BF, CF, DF and EF contain FR additives. The chlorobutyl rubber had a Mooney viscosity, ML 1 + 8 (125°C), of 45 to 52, unsaturation (mol%) of 2 and chlorine content (wt%) of 1.1 to 1.3. Antimony trioxide, ammonium polyphosphate and decabromodiphenyl oxide were used as FR additives. Carbon black type N339 was used for reinforcing purposes. Nickel dibutyldithiocarbamate was used as an antioxidant. END-75, which is 75% ethylene thiourea in a binder, zinc oxide and benzothiazyl disulfide were used as components of a cure system. Vistanex LM-MS, a polymer of isobutylene, and Carbowax 3350, a polyethylene glycol, served as processing aids. Sunpar 2280, a paraffinic oil, functioned as a plasticizer.

Table 2. Rubber formulations containing FR additives.

Ingredients	Formulation, Parts				
	AF	BF	CF	DF	EF
Formulation	A	B	C	C	C
Antimony trioxide	25	25	17	17	17
Ammonium polyphosphate	10	10	8	4	16
Decabromodiphenyl oxide	30	30	20	20	20

### Mixing and Sample Preparation

The rubber formulations were mixed on a laboratory two-roll mill and, subsequently, formed into sheets, measuring 6 inches by 6 inches and having thicknesses of 0.02 and 0.08 inches, by molding in a press for 60 minutes at 160°C.

### Test Procedures

Vulcanization characteristics of the rubber formulations were measured at 160°C using a Monsanto Oscillating Disk Rheometer R100. Minimum torque ( $M_L$ ), highest torque ( $M_H$ ), minutes to 2 units rise above  $M_L$  ( $t_2$ ) and minutes to 90% of highest torque [ $t_c(90)$ ] were calculated from the rheometer curves [3]. The highest torque attained, during a specified period of time was taken as  $M_H$ .

For flame resistance tests, 1 inch  $\times$  6 inch  $\times$  0.02 inch specimens were used. The specimens were exposed to a 3-inch-high flame by suspending them vertically in the flame for 12 seconds. Bunsen burner was used as the flame source. The specimen was held with the lower edge 2.8 inches above the center of the burner. Afterglow time was noted and length of uncharred part of the specimen was measured. Percent of test specimen consumed by flame was calculated using the following formula:

$$\text{Percent Consumed} = \frac{L - A}{L} \times 100$$

where

$L$  = original length of the specimen, inch

$A$  = length of uncharred part of the specimen, inch

Tensile strength (tensile stress at break), ultimate elongation (strain at break), tear resistance and 100%, 200% and 300% modulus (stress values at 100%, 200% and 300% strain, respectively) were determined using an Instron Tester Model 1130 (ASTM Methods D412, Die C and D624, Die C). All these properties were determined at room temperature using a crosshead speed of 20 inches/minute. The tensile and tear specimens were cut from 0.08-inch-thick sheets. Hardness of the formulations was measured using a hand-held device made by Shore Instrument & Mfg. Co.

Sorption tests were done on disks cut from 0.02-inch-thick molded sheets with a 1-inch diameter die. The disks were immersed in 1,5-dichloropentane (DCP) to study the effect of DCP on rubber compounds. Periodically, the disks were withdrawn from the DCP, blotted to remove the liquid from their surfaces, weighed and then returned to the DCP. Diffusion coefficient and permeation rate (flux) were calculated from the weight change data using the following equations [4]:

$$D = \frac{0.049d^2}{t_{1/2}}$$

$$J = -D \frac{C_1}{d}$$

where

$D$  = diffusion coefficient,  $10^{-8} \cdot \text{cm}^2/\text{sec}$

$J$  = permeation rate (flux),  $10^{-8} \cdot \text{g}/\text{cm}^2 \cdot \text{sec}$

$d$  = thickness of specimen, cm

$C_1$  = equilibrium weight gain, gm/100 g

The parameters  $C_1$  and  $t_{1/2}$  were obtained from the weight gain (%) versus square root of time curves.

## RESULTS AND DISCUSSION

### Vulcanization Characteristics

Figure 1 shows that the Monsanto Rheometer curves for rubber formulations A and AF do not plateau. For each formulation, torque at 55 minutes was taken as  $M_H$ . The effect of FR additives on  $t_2$ ,  $t_c(90)$  and  $M_H - M_L$  is shown in Table 3. The data suggest that FR additives increased  $t_2$  and  $t_c(90)$ , and decreased  $M_H - M_L$ . Table 4 indicates that the ammonium polyphosphate content has little effect on vulcanization parameters  $t_2$ ,  $t_c(90)$  and  $M_H - M_L$ .

### Flame Resistance

The flame resistance properties of our rubber formulations are given in Tables 5 and 6. The specimens of the formulations containing no FR additives continued to burn after removal of the flame source and were completely consumed. On the other hand, the specimens of the for-

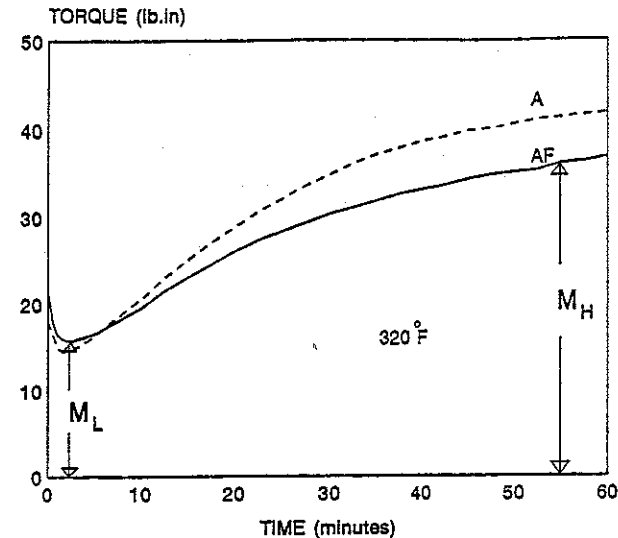


Figure 1. Monsanto Rheometer curves.

mulations containing FR additives were self-extinguishing and less than 10% of the specimen was consumed by flame. Table 6 indicates that the afterglow time and percent consumed decreased with increasing ammonium polyphosphate content.

Physical Properties

Figures 2 through 4 show that the stress values at 300% strain and at break decreased with the addition of flame retardants to the formulations. Moreover, the formulations with and without flame retar-

Table 3. Effect of FR additives on vulcanization characteristics of rubber formulations.

Formulation	$t_{s2}$ (minutes)	$t_c(90)$ (minutes)	$M_H - M_L$ (lb. in)
A	5.25	40.0	26.5
AF	7.25	44.0	20.3
B	6.0	38.5	23.5
BF	7.5	44.0	17.8
C	5.5	37.0	25.0
CF	7.0	43.0	19.0

Table 4. Effect of ammonium polyphosphate content on vulcanization characteristics of rubber formulations.

Formulation	Ammonium Polyphosphate (phr*)	$t_{s2}$ (minutes)	$t_c(90)$ (minutes)	$M_H - M_L$ (lb. in)
DF	4	6.8	43.5	19.3
CF	8	7.0	43.0	19.0
EF	16	7.0	42.5	17.5

\*Parts per hundred parts of rubber.

Table 5. Effect of FR additives on flame resistance of rubber formulations.

Formulation	Ignition	Percent Consumed	Afterglow Time (seconds)
A	propagates flame	100	—
AF	self-extinguishing	1.7	31
B	propagates flame	100	—
BF	self-extinguishing	5.0	37
C	propagates flame	100	—
CF	self-extinguishing	3.3	31

Table 6. Effect of ammonium polyphosphate content on flame resistance of rubber formulations.

Formulation	Ammonium Polyphosphate (phr)	Ignition	Percent Consumed	Afterglow Time (Seconds)
DF	4	self-extinguishing	9.4	42
CF	8	self-extinguishing	3.3	31
EF	16	self-extinguishing	2.2	16

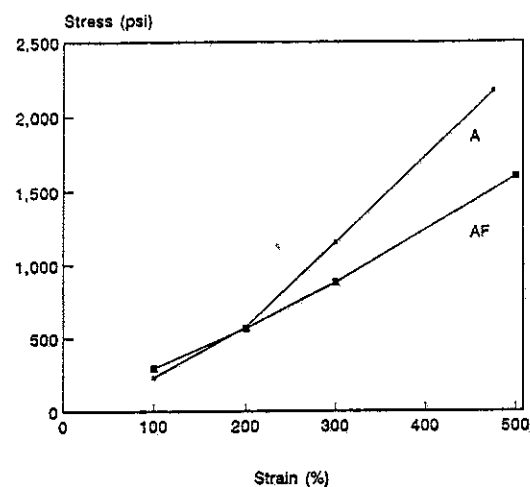


Figure 2. Effect of FR additives on strength properties.

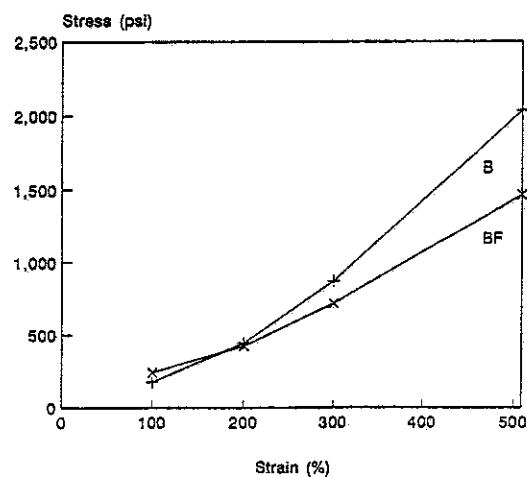


Figure 3. Effect of FR additives on strength properties.

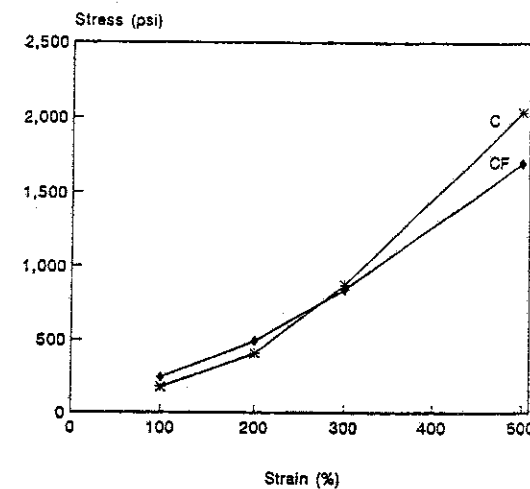


Figure 4. Effect of FR additives on strength properties.

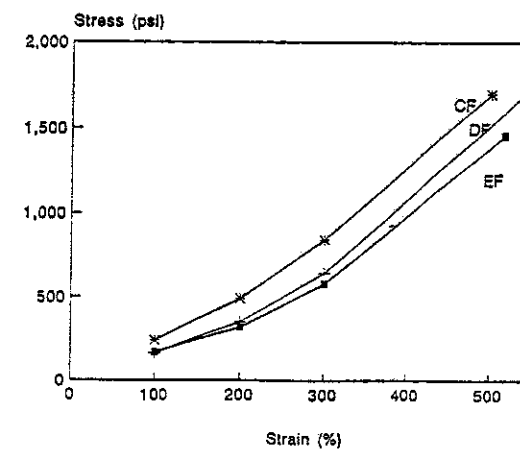


Figure 5. Effect of ammonium polyphosphate content on strength properties.

Table 7. Hardness and tear resistance of rubber formulations.

Formulation	Hardness (Shore A)	Tear Resistance (lb/in)
A	51	192
AF	59	180
B	48	165
BF	56	162
C	47	179
CF	55	165

dant additives have comparable stress values at 200% strain and comparable strain at break. Figure 5 displays the effect of ammonium polyphosphate content on the stress/strain behavior of rubber compounds. It indicates that the change in ammonium polyphosphate content, from 4 to 8 parts per hundred parts of a rubber (phr), increases the stress at 300% strain. The formulation containing 16 phr of ammonium polyphosphate exhibited the lowest stress at 300% strain and at break among the formulations containing 4, 8 and 16 phr of ammonium polyphosphate. The formulation containing 4 phr of ammonium polyphosphate exhibited the highest strain at break.

Hardness and tear resistance results are given in Tables 7 and 8. Table 7 points out that the formulations with FR additives have greater hardness but lower tear resistance values than the formulations without FR additives. Table 8 shows that the hardness increased with increasing ammonium polyphosphate content. The formulation containing 8 phr of ammonium polyphosphate exhibited the highest and the formulation containing 16 phr of ammonium polyphosphate exhibited the lowest tear resistance.

Figure 6 shows weight gain (%) versus square root of time curves for compounds A and AF immersed in DCP. The formulation with the FR

Table 8. Effect of ammonium polyphosphate content on hardness and tear resistance of rubber formulations.

Formulation	Ammonium Polyphosphate (phr)	Hardness (Shore A)	Tear Resistance (lb/in)
DF	4	50	141
CF	8	55	165
EF	16	56	135

Table 9. Effect of FR additives on diffusion coefficient and permeation rate of DCP for rubber formulations.

Formulation	Diffusion Coefficient ( $10^{-8}$ -cm <sup>2</sup> /sec)	Permeation Rate ( $10^{-8}$ -g/cm <sup>2</sup> -sec)
A	3.0	60.4
AF	2.7	47.2
B	4.4	86.5
BF	3.8	58.8
C	3.4	73.4
CF	2.6	51.7

additives (AF) has a lower maximum weight gain than the formulation without the FR additives (A). This difference is attributed to the polymer content. The formulation with the FR additives has a lower polymer content than the formulations without the FR additives. Diffusion coefficient and permeation rate data for a 0.01-inch-thick film of rubber are given in Tables 9 and 10. In general, the FR additives decreased the diffusion coefficient and permeation rate.

## CONCLUSIONS

FR additives were found to increase  $t_2$  and  $t_c(90)$ , and decrease  $M_H - M_L$ . However, ammonium polyphosphate does not have a significant effect on cure characteristics. Increase in  $t_2$  and  $t_c(90)$  indicates longer cure time. A combination of three FR additives, antimony trioxide, ammonium polyphosphate and decabromodiphenyl oxide, was found to give optimum balance between the physical properties and flame resistance. In general, the FR additives decreased the diffusion

Table 10. Effect of ammonium polyphosphate content on diffusion coefficient and permeation rate of DCP for rubber formulations.

Formulation	Ammonium Polyphosphate (phr)	Diffusion Coefficient ( $10^{-8}$ -cm <sup>2</sup> /sec)	Permeation Rate ( $10^{-8}$ -g/cm <sup>2</sup> -sec)
DF	4	2.9	64.0
CF	8	2.6	51.7
EF	16	3.1	56.0

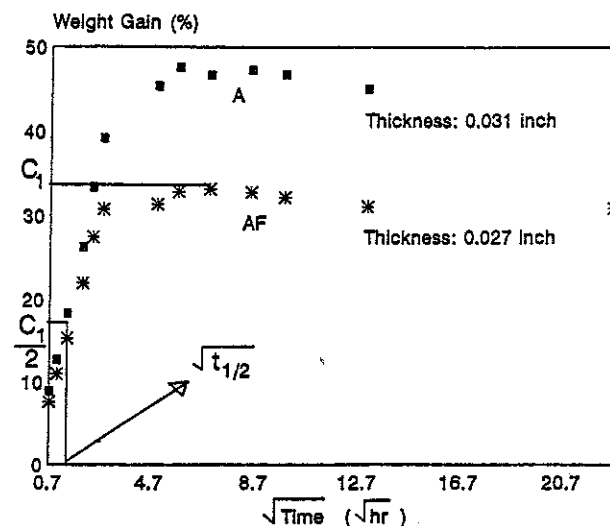


Figure 6. Weight gain in DCP for A and AF rubber formulations as a function of square root of time.

coefficient and permeation rate of the rubber formulations. In other words, the FR additives improved the barrier properties of the rubber formulations.

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# Phosphorus-Bromine Flame Retardant Synergy in a Polycarbonate/Polyethylene Terephthalate Blend

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**ABSTRACT:** The literature contains many claims to phosphorus/bromine flame retardant synergy. Many of these reports appear to be based upon a nonlinear response-concentration relationship. This paper shows convincing data for synergy in a 2/1 polycarbonate/polyethylene terephthalate blend. The literature also shows phosphorus efficiency as a flame retardant to be 3–8 times more effective than bromine, depending on the polymer and flame retardant. These data show phosphorus to be about ten times more effective than bromine in a 2/1 polycarbonate/PET blend. Brominated phosphates, where both bromine and phosphorus are in the same molecule, were also studied. In one case synergy is further enhanced when both phosphorus and bromine are in the same molecule. On a weight basis, phosphorus and bromine in the same molecule are perhaps the most efficient flame retardant combination.

**KEY WORDS:** flame retardants, phosphorus flame retardants, bromine flame retardants, synergy, phosphorus/bromine synergy, brominated phosphates, polycarbonate/polyethylene terephthalate blend, flame retarded engineering thermoplastics.

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